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THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIMETHYLTIN CHLORIDE AT--ETC(U)

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The Crystal and Molecular Structure of Trimethyltin Chloride
at 135 K. A Highly Volatile Organotin Polymer

by

M. Bilayet Hossain, J. L. Lefferts, K. C. Molloy,
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Trimethyltin chloride is the key starting material in the laboratory synthesis of the trimethyltin derivatives most subject to study. It is an article of commerce, and has itself been extensively studied by a great variety of spectroscopic and physical methods. There is in the literature starting in 1970 a trail of oft referenced private communications (see our ref. 16) which describe a yet unpublished X-ray structure which is incorrect. In addition, the structure of the analogous triphenyltin chloride, which is monomeric		

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at ambient temperature, is said to undergo a change on cooling to a chlorine-bridged polymer, but this suggestion is based upon NQR data at 77K which cannot be reproduced (see our ref. 5). The structure of the homologous trimethyltin fluoride cannot be solved because of disorder, and thus the widely-quoted bridging halide structures for R_3SnX compounds are being confirmed here in the case of the title compound for the first time. Solid trimethyltin chloride at 135K is associated through bent chlorine bridges into a one-dimensional polymer containing non-planar C_3Sn moieties in a distorted, axially-most electronegative, trigonal bipyramid at tin.



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at 135K. A Highly Volatile Organotin Polymer.

By M. Bilayet Hossain, J.L. Lefferts, K.C. Molloy, D. van der Helm* and J.J. Zuckerman*

(Department of Chemistry, University of Oklahoma, Norman, OK
73019 USA)

Summary Solid trimethyltin chloride at 135K is associated through bent chlorine bridges into a one-dimensional polymer containing non-planar C_3Sn moieties in a distorted, axially-most-electronegative, trigonal bipyramid at tin.

Trimethyltin chloride is a key laboratory starting material, an important article of commerce, and has been studied extensively by spectroscopic methods, yet the solid state structure of this highly toxic, low melting (m. $39.5^\circ C.$), volatile (b. $154^\circ C.$) material has never been determined because of experimental difficulties. The structure of the homologous trimethyltin fluoride,¹ which is associated through bridging fluorines, is perhaps the most widely quoted organotin structure of all,² yet disorder within and between the $-F-Sn-F-Sn-$ chains prevents a satisfactory solution to the anomalous electron density projections recorded at ambient temperatures.³ Triphenyltin chloride, on the other hand, exists as discrete, monomeric molecules in the crystal.^{4,5}

Crystals of trimethyltin chloride are monoclinic,

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$a = 12.541(8)$, $b = 9.618(11)$, $c = 11.015(11) \text{ \AA}$, $\beta = 92.62(7)^\circ$,
 space group P2, and $Z = 2$. Each asymmetric unit consists of
 four molecules. The structure was solved from 2183 indepen-
 dent reflections [$2\theta \leq 53^\circ$, Mo K_α radiation $I > 2\sigma(I)$] recorded at
 $135 \pm 2 \text{ K}$ on a Nonius CAD-4 counter diffractometer by the heavy-
 atom technique, and refined to a final R value of 0.069 (weigh-
 ted = 0.058). Sublimation of the crystals prevented the mea-
 surement of all faces, and thus no corrections for absorption
 could be made.

The stereochemistry of the asymmetric unit is shown in
 the Figure, along with mean values of the bond distances and
 angles. The two tin-chlorine distances are not equivalent,
 with the intramolecular bond [mean value $2.434(5,18) \text{ \AA}$]⁹ consi-
 derably shorter than the intermolecular [mean value $3.259(5,11)$
 \AA], although the latter is significantly shorter than the sum
 of the respective van der Waals radii (3.85 \AA).¹⁰ Comparison
 with the parameters of the recent gas-phase electron diffrac-
 tion study¹¹ is shown in the Table along with data from the ana-
 logous $[(\text{CH}_3)_3\text{SnCl}_2]^-$ anion (gegen ion $[\text{Mo}_3(\text{h}^5\text{-C}_5\text{H}_5)_3\text{S}_4]^+$) which
 takes an axially distorted, trigonal bipyramidal structure with
 one Sn-Cl the longest such intramolecular distance yet report-
 ed.¹²

The Cl-Sn-Cl-Sn-fragment is nearly linear at tin

[mean Cl-Sn-Cl angle $176.8(2,3)^\circ$], but bent at chlorine [mean angle $150.9(45)^\circ$], imposing a zig-zag character to the polymeric backbone, as in trimethyltin methoxide. However, in the latter case the trimethyltin moieties are staggered [the methoxyl methyl group eclipses an intermolecularly attached $(\text{CH}_3)_3\text{Sn}$ methyl]¹², while the trimethyltin units in the $(\text{CH}_3)_3\text{SnCl}$ chain are eclipsed. Single -Sn-Cl-Sn-bridges such as those found here may also appear in the structure of diphenyltin dichloride¹⁴ which has been reinterpreted in terms of chlorine asymmetrically bridging four- and six-coordinated tin atoms (intra- 2.353, inter- 3.78 \AA).¹⁴

The intermolecular tin-chlorine association in $(\text{CH}_3)_3\text{SnCl}$ is apparently disrupted on melting or dissolving in CS_2 as shown by reduced infrared and Raman $\nu(\text{Sn-Cl})$ values.^{16,17}

Acknowledgement. Our work is supported by the Office of Naval Research (JJZ) and the National Cancer Institute, DHEW, CA 17562 (DvdH).

References and Notes

1. H.C. Clark, R.J. O'Brien and J. Trotter, J. Chem. Soc., 1964, 2332.
2. J.A. Zubieta and J.J. Zuckerman, Prog. Inorg. Chem., 1978, 24, 251.
3. K. Kasuda, Y. Kawasaki, N. Kasai and T. Tanaka, Bull. Chem.

Soc. Jap., 1965, 38, 1216.

4. N.G. Bokii, G.N. Zakharova and Y.T. Struchkov, J. Struct. Chem. USSR, 1970, 11, 828.
5. The suggestion of a phase transition occurring in triphenyltin chloride between ambient and liquid nitrogen temperatures⁴ is based upon a very low value reported for the NQR coupling constant at 77K.⁶ However, this signal could not be reproduced by later workers.⁷ The close similarity of the Mössbauer parameters at 80, 110 and 295K strongly suggest that triphenyltin chloride is isostructural over this temperature range.⁸
6. T.S. Srivastava, J. Organomet. Chem., 1967, 10, 373.
7. N.W.G. Debye and M. Linzer, J. Chem. Phys., 1974, 61, 4770.
8. G.M. Bancroft, K.D. Butler and T.K. Sham, J. Chem. Soc., Dalton Trans., 1975, 1483.
9. Figures within parentheses refer to the standard deviation of a single observation and the r.m.s. deviation of the four independent measurements, respectively.
10. A. Bondi, J. Phys. Chem., 1964, 68, 441.
11. B. Beagley, K. McAloon and J.M. Freeman, Acta Cryst., 1974, B30, 444.
12. P.J. Vergamini, H. Varenkamp and L.F. Dahl, J. Am. Chem. Soc., 1971, 93, 6327.

13. A.M. Domingos and G.M. Sheldrick, Acta Cryst., 1974, B30, 519.
14. P.T. Greene and R.F. Bryan, J. Chem. Soc., (A), 1971, 2549.
15. N.G. Bokii, Yu. T. Struchkov and A.K. Prokofiev, J. Struct. Chem., USSR, 1972, 13, 619
16. H. Kriegsmann and S. Pischtschan, Z. Anorg. Chem., 1961, 308, 212.
17. Reports of an earlier X-ray structure by A.G. Davies, H.J. Milledge and D.C. Puxley showing a five-coordinated structure bent at tin have been quoted in the literature,¹⁸ but never published.
18. N.W. Alcock and J.F. Sawyer, J. Chem. Soc. Dalton Trans., 1977, 1090; M.T.P. Internat. Rev. Sci., 1972, 4, 280; R.V. Parish and R.H. Platt, Inorg. Chim. Acta, 1970, 4, 65.

Table

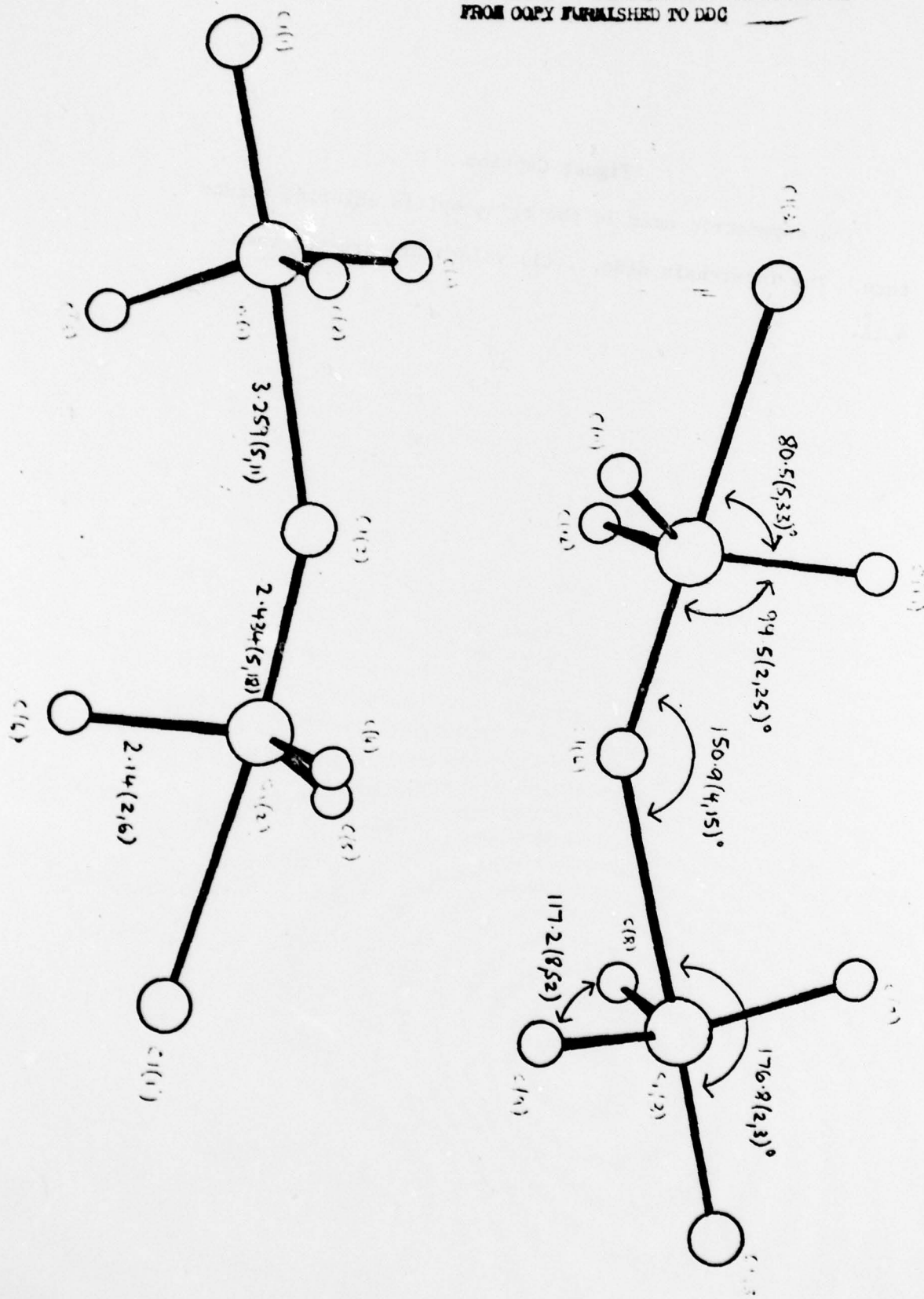
	<u>d(Sn-C)</u>	<u>d(Sn-Cl)</u>	<u><C-Sn-C</u>	<u><C-Sn-Cl</u>	<u>d(Sn---Cl)</u>	<u><(Cl-Sn---Cl)</u>
$(\text{CH}_3)_3\text{SnCl}^a$ X-ray at 135K	2.14(2,6) Å	2.434(5,18) Å	117.2(8,52)°	99.5(5,25)° intra- 80.5(5,33)° inter-	3.259(5,11) Å	176.8(2,3)°
predicted ^b	--	--	118°	99°	3.54	--
e.d. at 90°C ^c	2.106±0.006	2.351±0.007	114.9±1.6°	103.2±0.6°	--	--
$[(\text{CH}_3)_3\text{SnCl}_2]^{d\prime\prime}$ X-ray at R.T. ^d	2.12	2.572(4) 2.696(3)	--	--	--	--

^aThis work.^bR.F. Zahrobsky, J. Solid State Chem., 1973, 8, 101.^cRef. 11^dRef. 12

Figure Caption

The asymmetric unit in the trimethyltin chloride structure. The interchain $d(\text{Sn} \cdots \text{Cl})$ values are greater than 4.1\AA .

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STATEMENT

Trimethyltin chloride is the key starting material in the laboratory synthesis of the trimethyltin derivatives most subjected to study. It is an article of commerce, and has itself been extensively studied by a great variety of spectroscopic and physical methods. There is in the literature starting in 1970 a trail of oft referenced private communications (see our ref. 17) which describe a yet unpublished X-ray structure which is incorrect. In addition, the structure of the analogous triphenyltin chloride, which is monomeric at ambient temperature, is said to undergo a change on cooling to a chlorine-bridged polymer, but this suggestion is based upon NQR data at 77K which cannot be reproduced (see our ref.5). The structure of the homologous trimethyltin fluoride cannot be solved because of disorder, and thus the widely-quoted bridging halide structures for R_3SnX compounds are being confirmed here in the case of the title compound for the first time.